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DIENYL AND HOMODIENYL 1,5-HYDROGEN SHIFTS (1)

David S. Glass (2a), Robert S. Boikess (2b) and S. Winstein

Contribution No. 1893 from the Department of Chemistry
University of California, Los Angeles, California 90024

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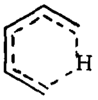
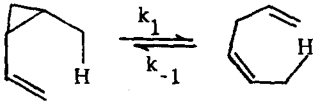
We reported recently (3a) that relatively facile intramolecular dienyl and homodienyl 1,5-hydrogen shifts occur in eight-membered cyclic trienes and their homo-counterparts. These 1,5-hydrogen shifts were symbolized by Ia ⇌ Ib and III ⇌ IV, by way of the delocalized six electron transition states IIa and Va, respectively.

Ia Ib



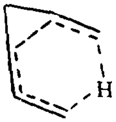
IIa

IIb

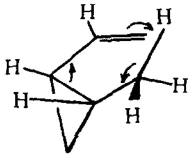


III IV

		Ref. 5a	Ref. 6
$\Delta H_1^{\ddagger}$	=	30.3	30.2
$\Delta S_1^{\ddagger}$	=	-12 e.u.	-11 e.u.

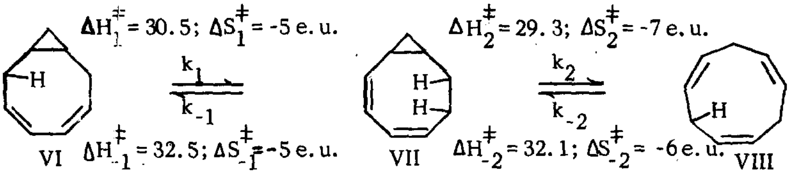


Va



Vb

The homodienyl 1,5-hydrogen shifts were the more novel and they appeared synthetically useful for the preparation of cis-cis-1,4-diene systems. An important example is the preparation of cis-cis-cis-1,4,7-cyclononatriene VIII from bicyclo(6.1.0)nona-2,4-diene VII (3, 4b).



$\Delta H_1^{\ddagger} = 30.5$; $\Delta S_1^{\ddagger} = -5$ e.u.

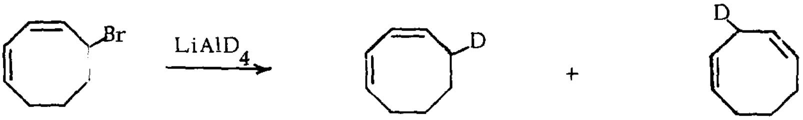
$\Delta H_2^{\ddagger} = 29.3$; $\Delta S_2^{\ddagger} = -7$ e.u.

VI $\Delta H_{-1}^{\ddagger} = 32.5$; $\Delta S_{-1}^{\ddagger} = -5$ e.u.

VII $\Delta H_{-2}^{\ddagger} = 32.1$; $\Delta S_{-2}^{\ddagger} = -6$ e.u. VIII

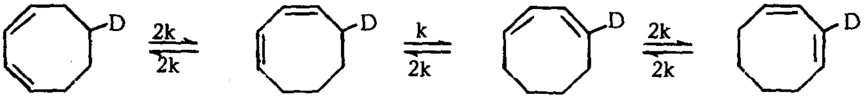
Recent work by us and others (4-14) has provided greater insight into the nature and scope of these 1,5-hydrogen shifts. These studies allow for comparison between dienyl and homodienyl cases in similar systems, and also between cyclic cases and open-chain analogs.

For comparison with the dienyl 1,5-hydrogen shifts in cyclooctatrienes and their monomethylene adducts VI and VII, we have studied the corresponding 1,5-shift in 1,3-cyclooctadiene using the monodeuterated 1,3-cyclooctadiene-5-d Xb. The latter compound, 99.6% monodeuterated, was separated from the mixture of 1,3-(40%) and 1,4-(60%) cyclooctadienes obtained by reduction of 1-bromo-2,4-cyclooctadiene IX (15) with lithium aluminum deuteride (16). The deuterated cyclooctadiene Xb showed signals in its n.m.r. spectrum for four vinyl protons (V) at 4.37 τ, three allylic protons (A) at 7.80 τ and four methylene protons (M) at 8.48 τ, with relative intensities V:A:M equal to 1:0.75:1. Its infrared spectrum showed methylene C-D stretching frequencies at 2180, 2158, 2132 (strong), 2115 (weak) cm.$^{-1}$



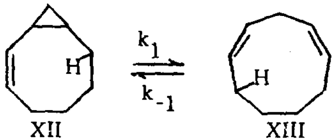
IX Xb XI

The neat liquid cyclooctadiene Xb, after heating at 150° for 24 hours, showed a new C-D stretching frequency at 2220 $cm.^{-1}$ in its infrared spectrum, and the V:A:M proton ratios had become 1:1:1, demonstrating an equilibration of the deuterium label throughout the molecule. The kinetics of this equilibration followed on neat liquid samples at 125.3, 137.1 and 150.2° by careful integration of the relative peak areas of the n.m.r. spectrum at various intervals were consistent only with a series of successive intramolecular 1,5-hydrogen shifts. For a monodeuterated 1,3-cyclooctadiene the dienyl 1,5-shifts which affect the n.m.r. spectrum are depicted as Xa ⇌ Xb ⇌ Xc ⇌ Xd. The rate constant k is defined for a single hydrogen transfer and secondary deuterium isotope effects are neglected.



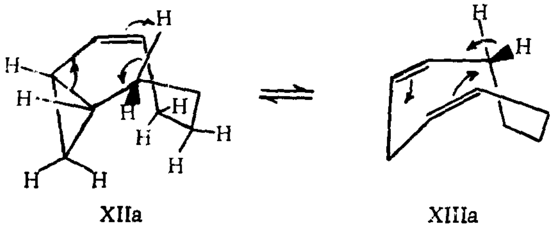
$\Delta H^\ddagger = 29.3$

$\Delta S^\ddagger = -10$ e.u.



$\Delta H_1^\ddagger = 31.4$

$\Delta S_1^\ddagger = -6$ e.u.



The kinetics of the three reversible first-order reactions can be treated to obtain the concentration of each deuterium species as a function of time t. The observed n. m. r. peak ratios are functions of the concentration of the four deuterated species and can be expressed in terms of the rate constant k and time t. By setting x equal to e^{-kt} one obtains:

$$y_1 = \frac{M}{A} = \frac{55 - 2x + 5x^4 + 2x^6}{55 - x - 5x^4 - 4x^6}$$

$$y_2 = \frac{V}{A} = \frac{55 + 3x + 2x^6}{55 - x - 5x^4 - 4x^6}$$

$$y_3 = \frac{M+A}{V} = \frac{110 - 3x - 2x^6}{55 + 3x + 2x^6}$$

As t increases from o to infinity, x decreases from 1.00 to 0. For this range of t, y_1 and y_2 range from 1.33 to 1.00, and y_3 ranges from 1.75 to 2.00. Rate constants derived from the variation of the observed ratios y_1, y_2 and y_3 with time are 3.46 (±1.06) x 10^{-5} sec.^{-1} at 150.2°, 1.42 (±0.37) x 10^{-5} sec.^{-1} at 137.1°, and 3.64 (±1.14) x 10^{-6} sec.^{-1} at 125.3°, leading to $\Delta H^{\ddagger}$ = 29.3 kcal/mole, $\Delta S^{\ddagger}$ = -10e.u. A single point gas-phase equilibration led to a similar rate constant, k being 3.08 (±0.70) x 10^{-5} sec.^{-1} at 161 ± 2° C.

The kinetics of the analogous homodienyl 1,5-hydrogen shift, the rearrangement of bicyclo(6.1.0)nona-2-ene XII to cis-cis-1,4-cyclononadiene XIII (17a) have also been studied. The n.m.r. spectrum of the bicyclononene XII shows a single high field cyclopropyl proton at 10.11 τ, bands due to eleven protons at 9.18 τ and 8.19 τ, and two vinyl protons at 4.46 τ.

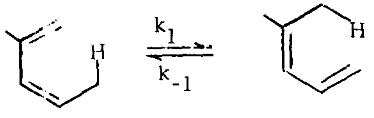
The cis-cis-1,4-cyclononadiene XIII, prepared by pyrolysis of XII and purified by v.p.c., shows bands in its n.m.r. spectrum at 8.49 τ for four methylene protons, 7.82 τ for four allylic protons and 7.22 τ for two bisallylic protons. Four vinyl protons appear at 4.53 τ. Bicyclo(6.1.0)nona-2-ene XII isomerizes smoothly to cis-cis-1,4-cyclononadiene XIII between 150 and 170°C.

Kinetics at 151.7° and 170.1° followed by n.m.r. using neat liquid samples led to $(k_1 + k_{-1}) = 1.25\ (\pm 0.07) \times 10^{-4}$ sec.$^{-1}$ at 170.1° and $2.56\ (\pm 0.12) \times 10^{-5}$ sec.$^{-1}$ at 151.7°C. The isomerization is reversible with $K = (k_1/k_{-1})$ equal to 82.3 at 170.1°, and the kinetics correspond to $\Delta H^{\ddagger}_1 = 31.4$ kcal/mole and $\Delta S^{\ddagger}_1 = -6$ e.u. A single point gas-phase rate at 150 ± 2°C. gave $k = 4.85 \times 10^{-6}$ sec.$^{-1}$, very close to the value for the liquid phase.

It is evident that the dienyl 1,5-shift in cyclooctadiene X and the homodienyl shift in the bicyclononene XII occur with very similar energies and entropies of activation. Further, these thermodynamic quantities are quite similar to those for the dienyl and homodienyl 1,5-shifts in the cyclooctatrienes (3a) and their monomethylene adducts VI and VII for which more quantitative data are now listed.

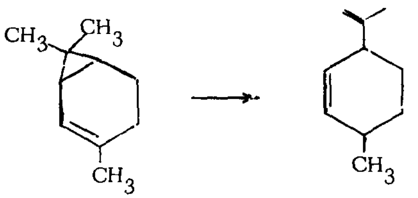
The activation parameters for these dienyl and homodienyl 1,5-hydrogen shifts in the eight-membered ring compounds are actually quite similar to values obtained for the corresponding dienyl 1,5-shifts by us (13) and by Frey and Ellis (5b) for the open chain system, cis-2-methyl-1,3-pentadiene XIV ⇌ 4-methyl-1,3-pentadiene XV, and for the homodienyl 1,5-shift by Frey and Ellis (5a) and Roth and König (6) for the system cis-1-methyl-2-vinylcyclopropane III ⇌ cis-1,4-hexadiene IV. In addition, Ohloff (7) has recently reported similar values for the rearrangement of 7,7-dimethylnorcarene derivatives to isopropenylcyclohexenes (e.g. XVI → XVII).

Considering the geometry of the transition state for these dienyl 1,5-hydrogen shifts, we had supposed that the arrangement of nuclei would tend to be as in IIb, the migrating hydrogen atom being situated above the approxi-



XIV XV

	Ref. 5b	Ref. 13
$\Delta H^{\ddagger}_1 =$	32.0	32.0
$\Delta S^{\ddagger}_1 =$	-8 e.u.	-9 e.u.

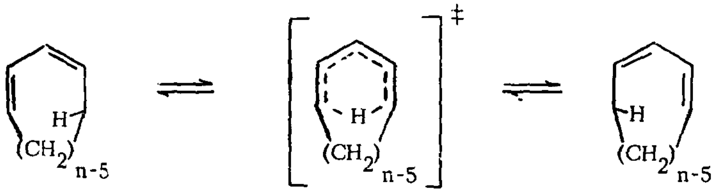


XVI XVII

$\Delta H^{\ddagger} = 27.2$

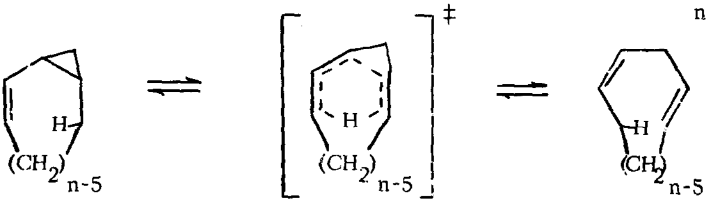
$\Delta S^{\ddagger} = -17$ e.u.

mate plane of the pentadienyl system and in a plane through the two terminal carbon atoms approximately perpendicular to the first plane. This type of arrangement (suprafacial) has recently been predicted by Woodward and Hoffman (18) from molecular orbital symmetry considerations and it is supported by extended Hückel calculations by Simonetta (19) and Woodward and Hoffman (18). Some tendency away from complete planarity of the five carbon system may be required to best accommodate the various orbital overlap requirements, especially in cyclic systems. In the case of the homodienyl 1,5-hydrogen shift the transition state can best be rationalized in terms of the non-planar conformation Vb. Models indicate that this conformation is the most favorable for overlap of the developing p-orbitals derived from the cyclopropane ring bond with the olefinic group and also the developing p-orbital derived from the C-H bond. On this basis, it is interesting to compare dienyl and homodienyl hydrogen shifts in various sized rings, depicted by XVIIIa ⇌ XVIIIb and XIX ⇌ XX, and in open-chain cases with no connecting polymethylene bridge between the terminal carbon atoms of the rearranging system.



XVIIIa XVIIIb

n ≡ ring siz



XIX XX

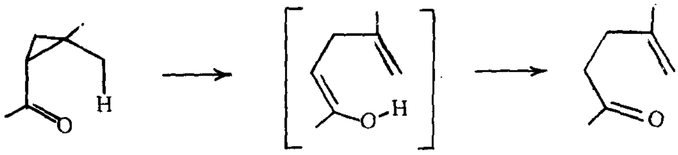
The dienyl 1,5-hydrogen shifts have comparable rates and activation energies in six (8), seven (9), eight (3,4) and nine (10) membered rings and in open-chain cases (5b, 7a). However, the activation energy is exceptionally low and the rate is correspondingly high in the 5-ring cyclopentadiene case. Quantum mechanically, the latter system is unique, since the pentadienyl system (18, 19) is now a closed cyclopentadienyl one, resulting in a quite different molecular orbital pattern from the former case. Sterically also, the cyclopentadiene system is unique since it does not have the steric interaction between the "inside" hydrogen atoms on C_1 and C_5 of a pentadienyl system which is unfavorable to the best transition state geometry.

For homodienyl 1, 5-hydrogen shifts, the required conformation (Vb, XIIa) can be achieved in both open-chain and eight membered ring cases, and the corresponding rates and activation energies are comparable. In the eight-membered case, a somewhat unfavorable saddle conformation (XIIa) is required in which there is some interaction of a cyclopropyl hydrogen atom with the opposite side of the ring (cf. ref. 3, 4). It is important to note that the migrating hydrogen atom is trans to the cyclopropane methylene group, both new olefinic groups created by the hydrogen shift having the cis configuration. Substituents on C_9 of a bicyclononene or bicyclononadiene system are unfavorable to the saddle conformation, and it is interesting that 9, 9-substituted bicyclo(6. 1. 0)nona-2, 4-diene derivatives (20) are quite stable, in contrast to the relative facility of the rearrangement of bicyclo(6. 1. 0)nona-2, 4-diene VII to 1, 4, 7-cyclononatriene VIII.

Models indicate that in the seven-membered ring case the hydrogen interaction with the opposite side of the ring becomes more serious in the saddle conformation required for the homodienyl shift. Further, the decrease in ring size tends to tip the olefinic group away from the migrating hydrogen atom. In fact, a high activation energy ($\Delta H^{\ddagger}$ = 38 kcal/mole) has been reported (12), leading to a $\Delta\Delta H^{\ddagger}$ of ca. 7 kcal/mole for the difference in activation energy between dienyl (9) and homodienyl (12) 1, 5-hydrogen shifts in seven-membered rings. In six-membered ring derivatives (XIX, n = 6) pyrolysis at 310°C. leads to slow rearrangement to products of which less that 1% can be explained by a homodienyl 1, 5-hydrogen shift (14). For bicyclo(3. 1. 0)-hexene (XIX, n = 5) no isomerization (<0.2%) occurs after 68 hours at 220°C., indicating a maximum rate constant of 7.8×10^{-9} sec.^{-1} at this temperature and $\Delta H^{\ddagger} > 44$ kcal/mole (assuming a typical entropy of activation of -7 e. u.). At higher temperatures both 1, 4- and 1, 3-cyclohexadienes are formed (13, 17b), possibly by a 1, 2-hydrogen shift. These results indicate a $\Delta\Delta H^{\ddagger} > 20$ kcal/mole for the difference in activation energy between dienyl and homodienyl 1,5-hydrogen shifts in cyclopentadiene and its homo-counterpart. The decreased ring size in both six- and five-membered rings is quite prohibitive to the non-planar conformation (c.f. Vb) required for the homodienyl shifts in these cases.

The activation parameters for dienyl 1,5-hydrogen shifts can be compared to the well-characterized 1,7-hydrogen shifts in the precalciferol ⇌ calciferol rearrangement and related compounds (21). The observed activation energy for these 1,7-hydrogen shifts (ca. 22 kcal/mole) suggests that when the hydrogen shift can be either 1,5 or 1,7 the 1,7-transition state tends to be favored by a substantial energy factor. However, all comparisons of this sort should take into account that ground-state free energy differences between the rearranging isomers in dienyl and homodienyl 1,5-shifts and in 1,7-shifts play a significant role in determining the activation energy requirements of the isomerizations.

One may conceive a number of structural variations of the systems undergoing dienyl and homodienyl 1,5-shifts. For example, thermal rearrangements via dienyl and homodienyl 1,5-hydrogen shifts have been reported for cases in which the terminal double bond is replaced by a carbonyl group. Kinetics on a homocarbonyl system, XXI → XXII (22), indicate that rates and activation parameters (calculated from rate data in reference 22) are comparable to those for homodienyl 1,5-hydrogen shifts in hydrocarbon systems.



XXI

XXII

$\Delta H^{\ddagger} = 27.5$

$\Delta S^{\ddagger} = -15$ e.u.

There is no reason to expect 1,5-shifts to be limited to hydrogen atoms and it is interesting that the n.m.r. behavior of certain σ-cyclopentadienyl organometallic derivatives suggests very facile thermal 1,5-shifts of the metallic group around the cyclopentadienyl nucleus (23). Examples of such systems are $(C_5H_5)_4Sn$ and $(C_5H_5)Si(CH_3)_3$ (23).

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(1) (a) Research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund; (b) reported in part at Eighth Annual Organic Chemistry Conference, U.S. Army Natick Laboratories, Natick, Mass., Oct. 13-14, 1964).

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